



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED

LAWRENCE
BERKELEY LABORATORY

NOV 24 1981

LIBRARY AND
DOCUMENTS SECTION

Engineering & Technical Services Division

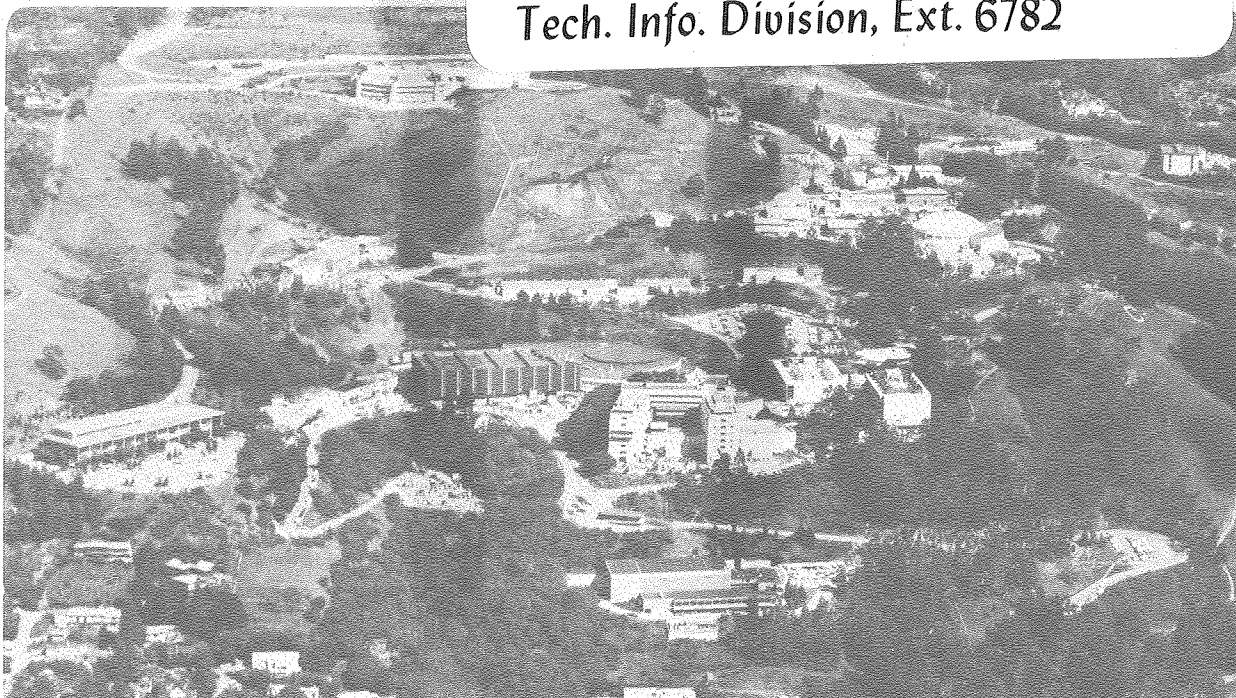
MILLIMETER AND SUBMILLIMETER WAVE ABSORPTION
BY ATMOSPHERIC POLLUTANTS AND CONSTITUENTS

W.F. Kolbe and B. Leskovar

October 1981

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782*



LBL-12236
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

MILLIMETER AND SUBMILLIMETER WAVE ABSORPTION BY ATMOSPHERIC POLLUTANTS AND CONSTITUENTS

W.F. Kolbe, B. Leskovar
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 U.S.A.

Abstract

Calculated absorption coefficients and rotational transition frequencies are given for a number of polar molecules of interest to pollution and energy research. The results, which are presented in graphical form for microwave frequencies up to 1400 GHz, illustrate the increased absorption line intensities occurring in the submillimeter region. For most species these absorption coefficients attain their maximum values in this region. Included in the calculations are the gases SO₂, H₂CO, O₃, H₂O, H₂S, OCS, CO, NO, OH, SO, NH₃, and CS. A discussion of the techniques currently available for the detection in the submillimeter region of these species is also given.

1. Introduction

Microwave rotational spectroscopy as a technique for the detection of trace concentrations of gaseous compounds and pollutants in air has been investigated by a number of researchers (1-3). Using these techniques several laboratory instruments (4-7) have been developed for the detection of specific species. Because of the relative technical simplicity of operating at low frequencies, most of these instruments have been designed to detect rotational transitions at frequencies below 35 GHz. However, as is well known (8), the absorption coefficients of most rotational transitions are significantly larger at higher microwave frequencies.

In this laboratory we have constructed a spectrometer (9,10) which operates in the vicinity of 70 GHz. With this instrument we are able to detect without pre-concentration specific molecules, for example, SO₂, OCS, with a limiting sensitivity approaching 1 ppm with a time constant of 1 second and somewhat greater sensitivities with longer time constants. While this sensitivity is sufficient for monitoring the concentration of pollutants in industrial environments and in the vicinity of pollution sources, it is inadequate for general pollutant detection under ambient conditions. In order to gain greater sensitivity, we are currently developing a spectrometer designed to operate at 140 GHz. Because the absorption coefficients at this frequency are significantly larger than at 70 GHz, we expect to demonstrate a considerable improvement in sensitivity.

In a previously published paper (11) we computed the absorption coefficients and transition frequencies for a number of molecular species of interest to pollution studies and energy research. The highest frequencies covered in this study were about 200 GHz. While the results clearly demonstrate the increase in absorption line intensities expected as the frequency is increased, it is evident that at even higher frequencies, in the submillimeter wavelength region, much larger absorption coefficients can be obtained. In fact, for most molecules at ambient temperatures, the maximum absorption coefficients (12) occur at frequencies of 1000 GHz or more. At these maxima the absorption coefficients are approximately 1000 times

larger than they are at 70 GHz. For this reason it would be very desirable to develop a spectrometer operating in this frequency region.

In the past, spectroscopy in the submillimeter region was extremely difficult because microwave sources of sufficient intensity and receivers of adequate sensitivity were not available. In recent years, however, significant improvements in technology have been made in both of the above areas. As a result, it is worthwhile to examine the submillimeter region as a potential candidate for the detection of pollutant species with high sensitivity.

In the next section, the equations describing the rotational absorption lineshapes and intensities are briefly reviewed. Peak absorption coefficients and transition frequencies for a number of species of interest are then presented in graphical form. Finally, we describe some of the methods currently available for the detection of rotational transitions in the submillimeter region.

2. Calculation of Absorption Coefficients

The absorption of microwave energy by a gas can be expressed in terms of the absorption coefficient, $\gamma(\nu)$. For frequencies, ν near a resonant absorption centered at frequency ν_0 , $\gamma(\nu)$ is given by (11,12)

$$\gamma(\nu) = \frac{8\pi^3 N f \nu^2}{3ckT} \left(1 - \frac{h\nu}{2kT}\right) |\mu_{ij}|^2 S(\nu, \nu_0) \quad (1)$$

where $|\mu_{ij}|^2$ is the square of the dipole matrix element associated with the transition, N is the number of molecules per unit volume of the sample, and f is the fraction of these in the lower energy state of the transition. T is the absolute temperature and k Boltzmann's constant. The normalized lineshape function $S(\nu, \nu_0)$ expresses the fact that the resonance has finite width.

In the absence of saturation, the two principal contributions to the linewidth come from collisional broadening and Doppler broadening. If the broadening due to collisional effects is dominant, the lineshape is Lorentzian and given by

$$S(\nu, \nu_0) = \frac{1}{\pi} \left[\frac{\Delta\nu_L}{(\nu - \nu_0)^2 + (\Delta\nu_L)^2} \right] \quad (2)$$

The linewidth, $\Delta\nu_L$, caused by bi-molecular collisions, is approximately proportional to the gas pressure. Since the concentration, N , is also proportional to pressure, the peak absorption at resonance,

$\gamma(v_0)$, obtained by combining equations (1) and (2) is pressure independent.

Under these conditions the peak absorption is given by (11,12):

$$\gamma_0 = \frac{8\pi^2\nu_0^2 |\mu_{ij}|^2 f}{3ckT} \left(\frac{N}{\Delta\nu_L} \right) \quad (3)$$

The ratio $N/\Delta\nu_L$ can be evaluated once the line width is known at a given pressure. If $(\Delta\nu)_1$, the line width (half width at half maximum), in MHz at one Torr and 300 K, is specified, we have:

$$\frac{N}{\Delta\nu_L} = 3.219 \times 10^{10} \frac{c}{(\Delta\nu)_1} \quad (4)$$

where c is the concentration of the species responsible for the transition.

The fraction, f , of molecules in the lower energy state of the transition can be written as the product $f = f_v f_r$. The fraction, f_v , of molecules in the vibrational state of interest can be calculated from the known vibrational frequencies of the molecule. For the ground vibrational state normally observed, the vibrational fraction, f_v , is of the order of unity at 300 K temperature. f_r and the remaining terms of the equation (1) must be computed from a diagonalization of the rotational Hamiltonian.

As the gas pressure is lowered and the frequency of observation is increased, the line width contribution due to the Doppler effect becomes significant. At the extreme Doppler limit, the line shape is Gaussian and is given by:

$$S(v, v_0) = \frac{1}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}} \exp \left\{ -(\ln 2) \left[\frac{v - v_0}{\Delta\nu_D} \right]^2 \right\} \quad (5)$$

The Doppler line width, $\Delta\nu_D$, is:

$$\Delta\nu_D = \frac{v}{c} \sqrt{2kN_0 \ln 2} \sqrt{\frac{T}{M}} \quad (6)$$

where k is Boltzmann's constant, N_0 Avogadro's number, T the absolute temperature and M the molecular weight. Since $\Delta\nu_D$ is proportional to frequency and inversely proportional to the square root of the molecular weight, the Doppler contribution to the line width is most important for high frequencies and light molecules.

As a typical example, for SO_2 at room temperature and a frequency of 1000 GHz, the Doppler line width (HWHM) is 0.78 MHz. If the pressure broadening line width parameter for SO_2 (11) is $(\Delta\nu)_1 = 16$ MHz/Torr, the Lorentzian and Doppler linewidth will be equal for

a pressure of 0.05 Torr. At this intermediate pressure the line shape can be approximated by the Voigt (13) function.

In order to ensure that the line shape is Lorentzian, the pressure-broadened line width should be several times the Doppler width. Under this condition the peak absorption coefficient will be pressure independent and, therefore, a convenient parameter to characterize the magnitude of the absorption.

3. Absorption Line Intensities

In this section the peak absorption coefficients and transition frequencies are given in graphical form for a number of gaseous species of environmental and energy related interest. Both stable species, such as SO_2 and H_2CO and unstable, free radical species, such as OH , are included in the compilation. The listed molecules are by no means all inclusive, and many more gaseous chemical species can, of course, be detected using microwave spectroscopic techniques.

In all cases, the peak absorption coefficients were obtained assuming a Lorentzian line shape. The peak intensities are thus inversely proportional to the pressure broadening line width parameter, $(\Delta\nu)_1$. In most cases the line width parameter used is that obtained for self-broadening and thus represents the line width for a 100% concentration of the gas. In dilute mixtures of pollutant gases in an air or other carrier, rotational relaxation of the detected species will take place predominantly through collisions of the gas molecules with the carrier and not with the species itself. Under this condition the line width parameter will often be considerably smaller (11) than it would be in a pure sample. The detected signal will then be proportionally larger.

The line width parameters also vary somewhat depending on the specific transition involved and, thus, the values presented are only average quantities. The most accurate way to obtain the actual absorption is to integrate the absorption signal over the entire line width.

The intensity data reported in all cases are for transitions involving the most abundant isotopic species in its ground vibrational state only. The results have been corrected for this by multiplying them by the relative abundance of this species and by the fractional population of the ground vibrational state at 300 K. The latter factor was computed (12) from the vibrational frequencies of the molecule for those cases where data were available.

3.1 Sulfur Dioxide

Because of its comparatively large dipole moment ($\mu = 1.634\text{D}$), SO_2 is a strong absorber in the microwave region. The transition frequencies and absorption coefficients were computed (14) by the present authors for all transitions up to 300 GHz. These results have been extended (using the same computer program) to 1400 GHz and are shown in Fig. 1. Only the strongest lines, namely those within an order of magnitude of the maximum, are shown.

Measurements of the line widths (14) of transitions in the vicinity of 35 GHz and 70 GHz yielded values ranging from 14 to 19 MHz/Torr. An average value of 16 MHz/Torr was used to obtain the results shown in the figure. The values shown were also corrected for the isotopic abundance of 94.5% for the principal isotope, $^{32}\text{S}^{16}\text{O}_2$, and the fractional occupation of the ground vibrational state at 300 K of

0.914. The results shown in the figure are in good agreement with those computed by Poynter and Pickett (15). A critical review of the microwave spectrum of SO_2 and its isotopes has been given by Lovas (16).

SO_2 is an asymmetric rotor with rotational constants which closely approximate a prolate symmetric rotor. As a result, the spectrum exhibits a well-defined series of Q-branches with approximately equal frequency spacing. The positions of the branches can be calculated (12) by solving the rigid rotor Hamiltonian in the prolate limit. The energy levels then become approximately

$$\frac{E}{h} = \frac{B+C}{2} J(J+1) + \left(A - \frac{B+C}{2} \right) K_{-1}^2 \quad (7)$$

where A, B, C, are the rotational constants and K_{-1} is the limiting prolate index of the level. For the Q-branch $\Delta J = 0$ and $\Delta K_{-1} = 1$. The branches occur at frequencies, f in GHz, given by:

$$f = \left(A - \frac{B+C}{2} \right) (K_{-1}^2 - K_{-1}^2) = 51.22 (2K_{-1} - 1) \quad (8)$$

The spacing is thus 102.4 GHz.

The Q-branches can be seen in Fig. 1 as a series of vertical dot patterns at approximately 100 GHz intervals. Since a large number of transitions occurs at nearly the same frequency in the vicinity of each Q-branch, a large absorption peak can be expected from their superposition. Figure 2 shows the calculated absorption spectrum for the $K_{-1} = 8$ Q-branch region. This spectrum was obtained by superimposing Lorentzian line shapes for each transition computed at a pressure of 10 Torr. The frequency and absorption coefficients of the individual lines were obtained from the calculated values of Poynter and Pickett (15). These lines are shown as small crosses in the figure.

In Fig. 3 a larger frequency region extending from 500 to 900 GHz is shown. A pressure of 50 Torr was assumed in calculating this spectrum. As can be seen, some of the Q-branch peaks are very nearly an order of magnitude larger than the individual lines surrounding them. A spectrometer operating in the vicinity of these peaks potentially offers greater sensitivity for detecting small concentrations of SO_2 .

Fleming (17) has measured the absorption spectrum of SO_2 over the spectral range 750 to 1250 GHz using a Fourier transform far-infrared spectrometer and obtained results in good agreement with the calculated spectrum (degraded to a resolution of $0.07 \text{ cm}^{-1} = 2.1 \text{ GHz}$). As he has shown, to accurately reproduce the observed spectrum, it is necessary to include contributions from $^{34}\text{SO}_2$ in the ground vibrational state (4%) and $^{32}\text{SO}_2$ in the first ν_2 vibrationally excited state (8%).

3.2 Formaldehyde

Measurements of the line width of a number of transitions below 35 GHz and near 70 GHz yielded (11) an average value of 22 MHz/Torr for the line width parameter. This value, plus an abundance of 98.6% for the principal isotope, and a ground state vibrational population of 0.99 were used to obtain the results shown in the figure.

Like SO_2 , formaldehyde (H_2CO) is a strong absorber ($\mu = 2.331\text{D}$) in the microwave region. Because of the large rotational constants ($A = 281,9070 \text{ MHz}$), however, there are fewer transitions in the accessible microwave region. Using the calculated values provided by Poynter and Pickett (15) absorption coefficients and transition frequencies for the strongest lines in the range 0 to 1400 GHz were obtained. The results are shown in Fig. 4.

3.3 Ozone

Although the electric dipole moment of O_3 is smaller ($\mu = 0.532\text{D}$) than SO_2 and H_2CO , the absorption lines are narrower. As a result, the peak absorption coefficients are comparable.

Using the calculated results of Poynter and Pickett (15), values were obtained for the frequencies and peak absorption coefficients of the more intense transitions. The results are shown in Fig. 5. For the line width parameter, $(\Delta\nu)_1$, a value of 4.6 MHz/Torr measured by Lichtenstein, et al (18) was used. Line width parameters for a number of O_3 transitions have also been computed by Tejwani and Yeung (19). The isotopic abundance of the principal isotope, $i_c = 0.993$ and for the ground state vibrational population, $f_v = 0.954$. The microwave spectrum and molecular parameters for O_3 and its isotopes have been critically reviewed by Lovas (16).

Like SO_2 , the sub-millimeter wave spectrum of O_3 exhibits number of strong Q-branches. Because of the larger rotational constants, however, the separation of these is about 188 GHz. Two of the absorption peaks resulting from the superposition of the lines in the vicinity of Q-branches is shown in Fig. 6. The O_3 line widths are quite narrow and a pressure of 100 Torr was selected in computing the absorption values. In fact, the peaks are still quite well resolved at one atmosphere of pressure, as shown in Fig. 7, where the same pressure broadening parameter was assumed.

3.4 Water Vapor

Because water is a very light molecule, the rotational constants are large and few transitions occur in the microwave region. In fact, only two lines (16), the 6_{16} to 5_{23} transition at about 22 GHz and the 3_{13} to 2_{20} transitions near 183 GHz occur below 300 GHz. Because of their influence on the atmospheric propagation of microwaves, these transitions have been studied extensively. The microwave spectrum of H_2O and its isotopes have been critically reviewed by Lovas (16).

Using the line width parameter of 18 MHz/Torr, measured for the 22 GHz transition by Liebe (20) and the calculated data of Poynter and Pickett (15), the peak absorption coefficients and transition frequencies for H_2O were obtained. The results are shown in Fig. 8.

3.5 Hydrogen Sulfide

Like water vapor, hydrogen sulfide is an extremely light molecule and comparatively few rotational transitions take place in the microwave region. The microwave spectrum of H_2S and its isotopes has been critically reviewed by Lovas (16).

Using an assumed line width parameter of 15 MHz/Torr and a relative abundance of 0.95 for the most common isotope, the peak absorption coefficients and frequencies were obtained from the calculations of Poynter and Pickett (15). The results are shown in Fig. 9.

3.6 Carbonyl Sulfide

Because of its stability, ease of handling and relatively intense microwave spectrum, carbonyl sulfide is often used (8) as a calibration source in microwave spectroscopy experiments. In addition, OCS is believed (21) to be an important source of sulfur in the stratosphere, where it participates in a number of photochemical reactions.

Using the molecular parameters compiled by Maki (22) and a linewidth parameter (11) of 6.4 MHz/Torr, the peak absorption coefficients and frequencies were computed for the most abundant isotope of this linear molecule. An isotopic abundance of 0.937 and ground state vibrational population of 0.828 were used. The results, which are plotted in Fig. 10, are identical to those computed by Poynter and Pickett (15).

At low frequencies, the absorption coefficients of this linear molecule increase as ν^3 . However, at 300 K a maximum is reached at about 475 GHz, after which the absorption decreases due to the decline in the thermal equilibrium populations of the lower states of the transitions.

3.7 Carbon Monoxide

Because carbon monoxide is a linear molecule with a large rotational constant, comparatively few transitions occur in the microwave region. Using an assumed linewidth parameter of 5 MHz/Torr and molecular parameters summarized by Lovas (23) the peak absorption coefficients and transition frequencies were computed for frequencies up to 1400 GHz. The results are shown in Fig. 11. Similar values were obtained by Poynter and Pickett (15).

The intensities of CO absorption lines increase with frequency as do those of OCS. However, the maximum absorption at 300 K temperature occurs at a frequency of 1497 GHz, beyond the range of Fig. 11.

3.8 Nitric Oxide

The nitric oxide molecule possesses an unpaired electron with orbital and spin angular moment $L = 1$ and $S = 1/2$, resulting in a $^2\Pi$ electronic ground state (12). The electronic spin-orbit interaction splits the ground state into a $^2\Pi_{1/2}$ level and a $^2\Pi_{3/2}$ level lying approximately 120 cm^{-1} above it. To a first approximation the molecular wave functions can be described by a Hund's case (a) representation in which both L and S are tightly coupled to the molecular axis. The projections Λ and Σ of L and S along the molecular axis then combine with the rotational angular momentum of the molecule to form the total (exclusive of nuclear) angular momentum, J . The observed microwave spectrum results from electric dipole transitions in which $\Delta J = \pm 1$.

As a result of interactions between the rotational and electronic motions of the molecule both L and S are slightly decoupled from the molecular axis. This decoupling, which increases with J , leads to a splitting (Λ -doubling) of the levels. In NO the doubling is small, amounting to a few hundred MHz for the $^2\Pi_{1/2}$ level and considerably less for the $^2\Pi_{3/2}$ level. In addition, a further splitting of the levels occurs because of hyperfine interactions involving the ^{14}N nucleus. The molecular parameters for NO have been reviewed by Lovas and Tiemann (23).

Using the calculated frequencies and intensities provided by Poynter and Pickett (15) and a line width parameter of 3 MHz/Torr, peak absorption coefficients were obtained for the stronger transitions of NO. The results are shown in Fig. 12. The data lie along two smooth curves, with the higher intensity curve resulting from the $^2\Pi_{1/2}$ electronic state and the other arising from the $^2\Pi_{3/2}$ state. Only the strongest hyperfine transition is plotted in the figure.

3.9 Hydroxyl Radical

The electronic ground state of the hydroxyl radical is similar to that of nitric oxide. In OH, the spin-orbit splitting of the $^2\Pi$ ground state is reversed with the $^2\Pi_{1/2}$ level lying about 140 cm^{-1} above the $^2\Pi_{3/2}$ level. The rotational constant for OH is much larger than that of NO, and the decoupling of the electronic orbital momentum is more pronounced. This leads to a large Λ -doubling of each rotational level.

Since the OH radical is so light, its pure rotational spectrum lies in the far infrared. The lowest pure rotational transition, as calculated by Poynter and Pickett (15) occurs at about 1835 GHz. The observed transitions in the microwave region occur between the Λ -doublets and range in frequency from about 1 GHz to approximately 200 GHz, depending on the J value of the rotational state involved.

The peak absorption line intensities and frequencies for the Λ -doubling transitions obtained from Poynter and Pickett (15) are shown in Fig. 13. Similar results for the calculated intensities were obtained by the present authors (10). The frequencies and line widths of a number of transitions in the vicinity of 70 GHz were also measured (10) and the observed line width parameter of 3.1 MHz/Torr was used to obtain the peak absorption line intensity. In Fig. 13 only the strongest hyperfine component of each transition is shown.

3.10 Sulfur Monoxide

The electronic ground state of the sulfur monoxide radical is $^3\Sigma$, with $L = 0$ and net electronic spin $S = 1$. Each rotational level is split by interactions with the spin into a triplet with components designated by the total angular momentum quantum numbers $J = N-1$, N , $N+1$, where N is the rotational quantum number. The observed transitions are electric dipole with $\Delta J = 0$, ± 1 and $N = \pm 1$. Other transitions with $\Delta N \neq 1$, including magnetic dipole transitions are also permitted, but are weaker and have not been observed in laboratory measurements to date.

Using the calculated values of Poynter and Pickett (15) peak absorption coefficients are given in Fig. 14 for the strongest transitions. For most of the lines in the figure $\Delta J = \Delta N = 1$. An isotopic abundance of 0.95 for the principal isotope and a line width parameter of 5 MHz/Torr, as measured previously by the present authors (10) for SO diluted in an Ar carrier gas, were used.

3.11 Ammonia

The ammonia molecule, NH_3 , is a symmetric rotor with a pyramidal structure. The potential function for the molecule is such that the nitrogen atom is able to tunnel back and forth through the plane of hydrogen atoms. This inversion process takes place over a band of frequencies centered at about 23 GHz, with the individual frequencies depending upon the

particular rotational state involved due to centrifugal distortion effects. In addition to the inversion spectrum, rotation-inversion transitions also occur for ammonia. Because of its extremely small moment of inertia, however, the lowest frequency transition of this type occurs at approximately 572 GHz. The microwave spectrum, line parameters and spectral constants for ammonia have been described in some detail by Poynter and Kakar (24).

Using an average value of 25 MHz/Torr and the calculated values of Poynter and Pickett (15) peak absorption coefficients were obtained for the rotation-inversion transitions of NH_3 . These are shown in Table I. Also shown is the 3,3 inversion transition, strongest of the many inversion lines occurring in the low frequency spectral region.

Table I
Absorption Line Intensities for NH_3

Transition $J', K' - J'', K''$	Frequency GHz	Calculated Abs. Coef.
3,3 3,3	23.87	8.1×10^{-4}
1,0 0,0	572.50	1.3×10^{-1}
2,1 1,1	1168.43	3.5×10^{-1}
2,0 1,0	1214.83	1.0×10^0
2,1 1,1	1215.22	3.8×10^{-1}

3.12 Carbon Monosulfide

The unstable species carbon monosulfide, CS, has been shown to play a role in chemical reactions in the atmosphere involving sulfur compounds (21). Although CS is an unstable species, it is not a free radical, as are OH and SO, because the electronic ground state does not contain an unpaired electron. The ground state is $^1\Sigma$ and the molecule exhibits a simple spectrum characteristic of a linear rotor. The microwave spectral constants for CS have been summarized by Lovas and Tiemann (23).

Using the calculated values of Poynter and Pickett (15) and an assumed linewidth parameter of 5 MHz/Torr, the peak absorption coefficients for CS were obtained. An isotopic abundance of 0.94 for the principal isotope was used in computing the absorption coefficients. The results are shown in Fig. 15.

4. Detection of Submillimeter Rotational Transitions

Although the absorption coefficients of most molecules are considerably larger in the submillimeter region than they are at lower frequencies, the availability of spectrometers to detect them with high sensitivity is somewhat limited. In this section we will describe briefly some of the spectrometer systems and components employed in this frequency range.

As in the case of spectrometers operating at lower frequencies, the primary sources of noise which limit sensitivity (25) can be attributed to the source generator which excites the molecules and to the receiving device which detects the radiation. The state of the art of these components has been discussed recently by Blaney (26) and the reader is referred to this excellent overview for a more complete review.

4.1 Submillimeter Signal Sources

A major problem in the submillimeter region has been the development of tunable low noise sources of sufficient power output (26). At the low frequency end of the range conventional microwave sources, including klystrons and solid state devices (Gunn and impatt oscillators), are available. In the case of klystrons, frequencies up to about 200 GHz can be obtained. Backward wave oscillators have been used at frequencies up to about 1000 GHz. Unfortunately, the power output of these devices decreases rapidly as the frequency is increased. In addition to fundamental oscillators, harmonic generation from lower frequency sources has often been employed, although the power output available is quite low at the higher frequencies.

With the advent of electrically-excited and optically-pumped submillimeter-wave gas lasers, discrete frequencies (pulsed, and in some cases, CW) from more than a thousand transitions (27) have become available. Although these sources are essentially non-tunable, they have been employed in situations where accidental coincidences exist between the laser frequency and the molecular transition being investigated. In addition, Fetterman et al. (28), for example, have shown that tunable submillimeter frequencies (at power levels up to about 10^{-7} W) can be obtained by mixing the laser output with lower frequency microwaves using Schottky barrier diodes.

4.2 Signal Detection

In the area of signal detection, several types of receivers have been employed (26). These can be roughly grouped into three categories: rectifiers, in which the signal is detected through non-linear rectification processes; thermal devices, where the power absorbed is converted to heat and thence to a change in resistance; and photon devices, in which individual quanta of radiation release charge carriers, as in photoconductors.

At the low end of the frequency range, the most sensitive receivers have usually employed heterodyne detection in which the detected signal is mixed with microwave power from a local oscillator to produce an IF signal suitable for further amplification. With waveguide mixers and GaAs Schottky diodes, good performance has been obtained at frequencies up to 300 GHz. Promising results have also been obtained for frequencies up to about 1000 GHz employing open structures and whisker antennas (28). Very low noise operation has been obtained at frequencies up to 450 GHz using Josephson junction mixers. These devices have the disadvantage of requiring liquid helium for operation but can be made to work with very low local oscillator power.

Liquid helium-cooled, photoconductive devices employing, for example, indium antimonide coupled to the microwaves via a "light pipe," have been used successfully as video detectors (29) to detect microwave transitions at frequencies up to about 800 GHz. They have also been used in submillimeter Fourier transform spectrometers (17), as described below.

4.3 Spectrometer Systems

The first successful techniques for performing microwave spectroscopy on molecules at submillimeter frequencies were pioneered by Gordy and co-workers and have been recently reviewed by DeLucia (29). Microwave radiation is produced by high order harmonic

multiplication of the output of a millimeter-wave klystron. After passing through an absorption cell containing the gas under investigation, the microwave energy is detected by a low noise receiver, usually a liquid He-cooled indium antimonide photoconductor, as described above. The principal factor limiting the sensitivity at the highest frequencies (about 800 GHz) is the very small amount of microwave power available (much less than 1 μ W) from the harmonic multiplication process.

A quite different approach is employed by Krupnov and co-workers (30) to detect microwave transitions at frequencies up to about 1100 GHz. For their technique a backward wave oscillator is used as a signal source. However, the gas absorption is detected, not by measuring the change in power passing through the absorption cell, but by acoustically detecting pressure fluctuations within the cell. These result from the absorption of microwave power by the gas at the molecular resonance frequency and are detected by placing a special low noise microphone in a side port of the cell. The signal-to-noise ratio is improved by (frequency or amplitude) modulation of the microwave source and lock-in detection at the modulation frequency. The sensitivity of the acoustic detection method is moderate. Measurements of the rare isotopes of OCS in the vicinity of 360 GHz show that transitions with absorption coefficients of 10^{-5} cm^{-1} can be detected rather easily, the limiting sensitivity being perhaps 10^{-7} cm^{-1} . It is important to realize, however, that the sensitivity is proportional to the input power available from the microwave source. The same authors demonstrated a sensitivity of 10^{-11} cm^{-1} at 35 GHz, using a source power of 1 kW. Such powers are, unfortunately, not available at present in the submillimeter region, except, perhaps, with the essentially non-tunable laser sources.

By extending the techniques of infrared spectroscopy to lower frequencies Fleming (17) and others have developed Fourier transform spectrometers capable of measuring, with high precision, rotational transitions in the submillimeter region. In this method, the gas to be measured is placed in an absorption cell mounted in a motor-driven scanning interferometer. A continuum (thermal) source is used to illuminate the interferometer and a low-noise receiver, such as the indium antimonide detector mentioned above, detects the interference signals produced. After signal averaging, if necessary, the resulting interferogram is Fourier transformed to obtain the absorption spectrum.

The advantage of the above technique is that a single measurement suffices to obtain the complete spectrum of the gas over a wide frequency range, for example, from 300 to 1200 GHz. Conventional spectrometers would require hours or days of scanning with many different source oscillators to achieve the same bandwidth. The spectral resolution attainable is inferior to that of conventional spectroscopy, the best resolution being about 0.07 cm^{-1} or 2 GHz. The signal-to-noise ratio at each frequency interval in the spectrum is reduced relative to that attainable using conventional microwave sources because the power density in the continuum source is so low. However, high sensitivity for trace gas detection might be attainable by comparing the observed spectrum, using correlation techniques, to a sample spectrum obtained at higher concentration. Measurements of a number of species of interest to pollution and atmospheric studies, including H_2O , NO_2 , SO_2 , HNO_3 , H_3S , HCl , CF_3Cl , CF_2Cl_2 and O_3 have been made (17) using the Fourier transform technique.

Because of their high sensitivity at the low microwave power levels currently available in the submillimeter region, spectrometers employing coherent superhetrodyne detection offer considerable hope for the detection of low concentrations of pollutant species. Until recently, suitable mixers for superhetrodyne detection were limited to frequencies below a few hundred GHz. However, as described above, diode mixers have now been developed (28) which can be operated at frequencies up to about 1000 GHz. A spectrometer employing such a mixer has been described by Blumberg, et al (31). Tunable submillimeter radiation was obtained by mixing in a Schottky diode sideband generator, the output of a submillimeter laser with a lower frequency microwave source. After passing through an absorption cell containing the gas, the submillimeter waves were detected using the above mixer with the same laser radiation as a local oscillator. Successful operation was obtained at 403 and 653 GHz and many other frequencies are possible, depending on the availability of suitable laser lines.

5. Summary

Calculated absorption coefficients and rotational transition frequencies have been given for a number of polar molecules of interest to pollution and energy research. The results show the expected increase in the absorption line intensities in the submillimeter-wave region. In fact, for most species the absorption coefficients increase by a factor of approximately 1000 compared to their values in the millimeter region (50 - 70 GHz).

In the millimeter region, the sensitivity of detection is such that concentrations of about 1 ppm can be detected with a 1 sec. time constant. If detectors of comparable sensitivity were available at 1000 GHz, one would be able to detect a concentration of 1 ppb.

From the discussion of submillimeter-wave spectrometers presented above, it is apparent that while impressive improvements in technology have been made in recent years, much effort still remains to achieve the noise performance and sensitivity available at lower frequencies. Of the spectrometer systems discussed above, the apparatus described by Fetterman and Blumberg appears particularly promising. The noise temperature (10 000 K) of their receiver is not dramatically worse than that available (100 - 1500 K) at lower frequencies. Even if a factor of ten degradation in performance resulted in the 1000 GHz region, detection limits of 10 ppb with a 1 sec. time constant could be achieved. With longer time constants, even greater sensitivity could be obtained.

Acknowledgments

The authors would like to express their appreciation to Drs. R.L. Poynter and H.M. Pickett for supplying them with a computer tape of the results of their calculations which greatly facilitated the compilation of much of the data presented in this report.

This work was supported by the Assistant Secretary of the Environment, Office of Health and Environmental Research, Pollutant Characterization and Safety Research Division, U.S. Department of Energy, under Contract W-7405-ENG-48.

6. References

1. W.F. White, The Application of Microwave Spectroscopy to Contaminant Analysis, *Am. Inst. Chem. Engs.* **62**, 70 (1966).
2. J.T. Funkhouser, S. Armstrong and H.W. Harrington, *Analytical Chem.* **40**, 22A (1968).
3. L.W. Hrubesh, *Radio Science* **8**, 167 (1973).
4. L.W. Hrubesh, R. Anderson, E. Rinehard, *Rev. Sci. Instr.* **41**, 595 (1970).
5. H. Uehara, M. Tanimoto, Y. Ijuuin, *Chem. Phys. Lett.* **26**, 578 (1974); **28**, 597 (1974).
6. H. Uehara, Y. Ijuuin, Y. Morino, T. Kamidate, A. Nakamura and H. Imai, *Rev. Sci. Instr.* **51**, 334 (1980).
7. W. Schilz, B. Schiek, "Microwave Systems for Industrial Measurements," *Adv. in Electronics and Electron Physics*, **55**, 309 (1981).
8. C.H. Townes, A.L. Schawlow, *Microwave Spectroscopy*, McGraw-Hill, New York (1955).
9. W.D. Zoellner, W.F. Kolbe and B. Leskovar, *IEEE Trans. Nucl. Sci.*, **NS-27**, 719 (1980).
10. W.F. Kolbe, W.D. Zoellner and B. Leskovar, "Microwave Spectrometer for the Detection of Transient Gaseous Species," Lawrence Berkeley Laboratory Report, LBL-7293, June, 1979, and published in *Rev. Sci. Instr.*, **52**, 59 (1981). Also presented in part at the 34th Symposium on Molecular Spectroscopy, The Ohio State University, Columbus, Ohio, June 11-15, 1979.
11. W.F. Kolbe, H. Buscher and B. Leskovar, "Microwave Absorption Coefficients of Atmospheric Pollutants and Constituents," *J. Quant. Spectrosc. Rad. Transf.* **18**, 47 (1977).
12. W. Gordy, R.L. Cook, *Microwave Molecular Spectra*, Wiley (Interscience), New York (1970).
13. B.H. Armstrong, "Spectrum Line Profiles: the Voigt Function," *J. Quant. Spectrosc. Rad. Transf.* **7**, 61 (1967).
14. W.F. Kolbe, B. Leskovar and H. Buscher, "Absorption Coefficients of Sulfur Dioxide Microwave Rotational Lines," *J. Mol. Spectros.*, **59**, 86 (1976).
15. R.L. Poynter, H.M. Pickett, "Submillimeter, Millimeter and Microwave Spectral Line Catalogue," Jet Propulsion Laboratory Report, JPL-80-23, Revision 1, June 1981.
16. F.J. Lovas, "Microwave Spectral Tables. II. Triatomic Molecules," *J. Phys. Chem. Ref. Data* **7**, 1445 (1978).
17. J.W. Fleming, "Interferometric Spectrometry at Millimetre and Submillimetre Wavelengths" in *Modern Aspects of Microwave Spectroscopy*, G.W. Chantry, ed., Academic Press, London (1979).
18. M. Lichtenstein, J.J. Gallagher and S.A. Clough, "Millimeter Wave Spectrum of Ozone," *J. Molec. Spectrosc.* **40**, 10 (1971).
19. G.D.T. Tejwani, E.S. Yeung, "Pressure Broadened Linewidths of Ozone," *J. Chem. Phys.* **63**, 1513 (1975).
20. H.J. Liebe, M.C. Thompson, Jr., T.A. Dillon, "Dispersion Studies of the 22 GHz Water Vapor Line Shape," *J. Quant. Spectrosc. Rad. Transf.* **9**, 31 (1969); **11**, 1803 (1971).
21. D.L. Baulch, R.A. Cox, R.F. Hampson, Jr., J.A. Kerr, J. Troe, R.T. Watson, "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry," *J. Phys. Chem. Ref. Data* **9**, 295 (1980).
22. A.G. Maki, "Microwave Spectra of Molecules of Astrophysical Interest VI Carbonyl Sulfide and Hydrogen Cyanide," *J. Phys. Chem. Ref. Data* **3**, 221 (1974).
23. F.J. Lovas, E. Tiemann, "Microwave Spectral Tables I Diatomic Molecules," *J. Phys. Chem. Ref. Data* **3**, 609 (1974).
24. R.L. Poynter, R.K. Kakar, "The Microwave Frequencies, Line Parameters and Spectral Constants for $^{14}\text{NH}_3$," *Astrophys. J. Suppl. Series No. 277* **29**, 87 (1975).
25. B. Leskovar, D.B. Hopkins, W.F. Kolbe, "Optimal Design Criteria for Millimeter-Wave Spectrometers," *Proc. 5th European Microwave Conf.*, Sept. 1, 1975, pp. 228-232.
26. T.G. Blaney, "Detection Techniques at Short Millimeter and Submillimeter Wavelengths: An Overview," in "Infrared and Millimeter Waves, Vol. 3, Submillimeter Techniques," K.J. Button, ed., Academic Press, New York (1980).
27. R. Beck, W. Englisch and K. Gürs, "Table of Laser Lines in Gases and Vapors," *Springer Series in Optical Sciences*, Vol. 2, Springer-Verlag, Berlin (1978).
28. H.R. Fetterman, P.E. Tannenwald, B.J. Clifton, W.D. Fitzgerald and N.R. Erickson, "Far-ir Heterodyne Radiometric Measurements with Quasioptical Schottky Diode Mixers," *Appl. Phys. Lett.*, **33**, 151 (1978).
29. F.C. DeLucia, "Millimeter and Submillimeter-Wave Spectroscopy," in *Molecular Spectroscopy: Modern Research II*, K.N. Rao, ed., Academic Press, New York (1976).
30. A.F. Krupnov, A.V. Burenin, "New Methods in Submillimeter Microwave Spectroscopy," in *Molecular Spectroscopy: Modern Research II*, K.N. Rao, ed., Academic Press, New York (1976).
31. W.A.M. Blumberg, H.R. Fetterman, D.D. Peck and P.F. Goldsmith, "Tunable Submillimeter Sources Applied to the Excited State Rotational Spectroscopy and Kinetics of CH_3F ," *Appl. Phys. Lett.* **35** 582 (1979).

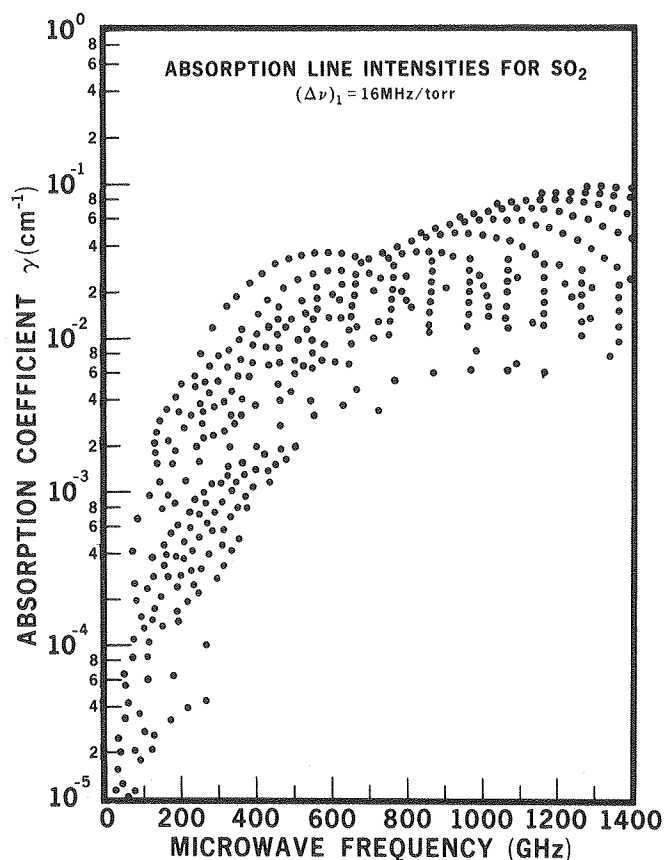


Fig. 1 Absorption coefficients for SO_2 computed assuming $T = 300 \text{ K}$, $(\Delta\nu)_1 = 16 \text{ MHz/Torr}$, $f_v = 0.917$ and $i_c = 0.945$.

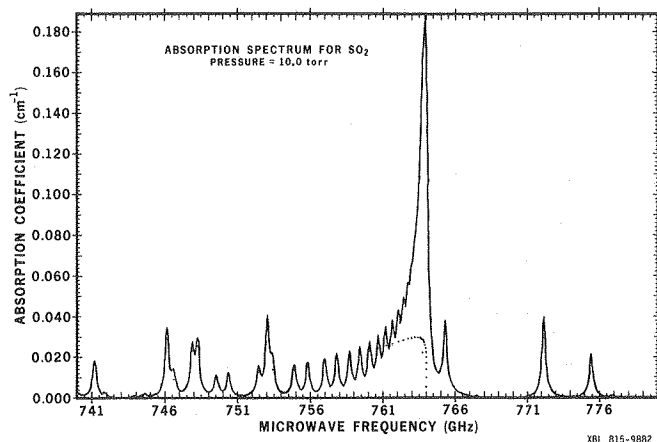


Fig. 2 Absorption spectrum for SO_2 near the $K_{-1} = 8$ Q-branch evaluated for a pressure of 10.0 Torr.

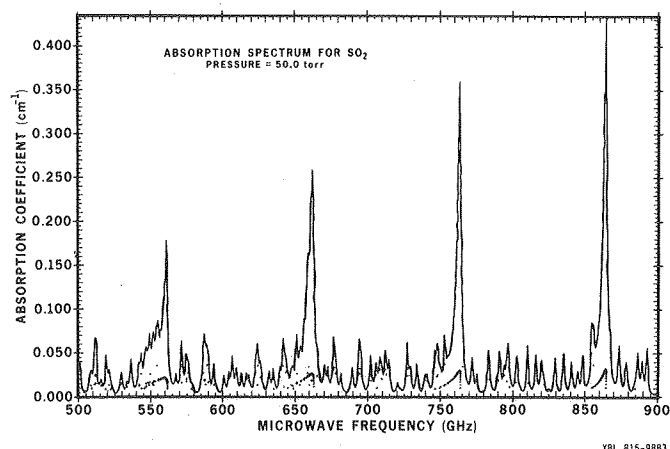


Fig. 3 Absorption spectrum for SO_2 at a pressure of 50 Torr showing several Q-branches in the frequency range of 500 to 900 GHz.

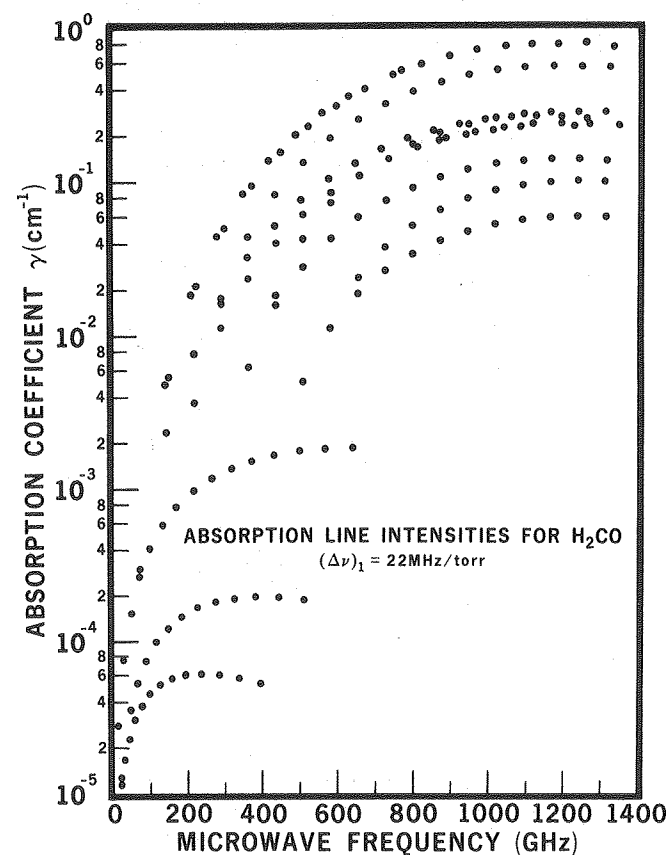


Fig. 4 Absorption coefficients for H_2CO computed assuming $T = 300 \text{ K}$, $(\Delta\nu)_1 = 22 \text{ MHz/Torr}$, $f_v = 0.99$ and $i_c = 0.986$.

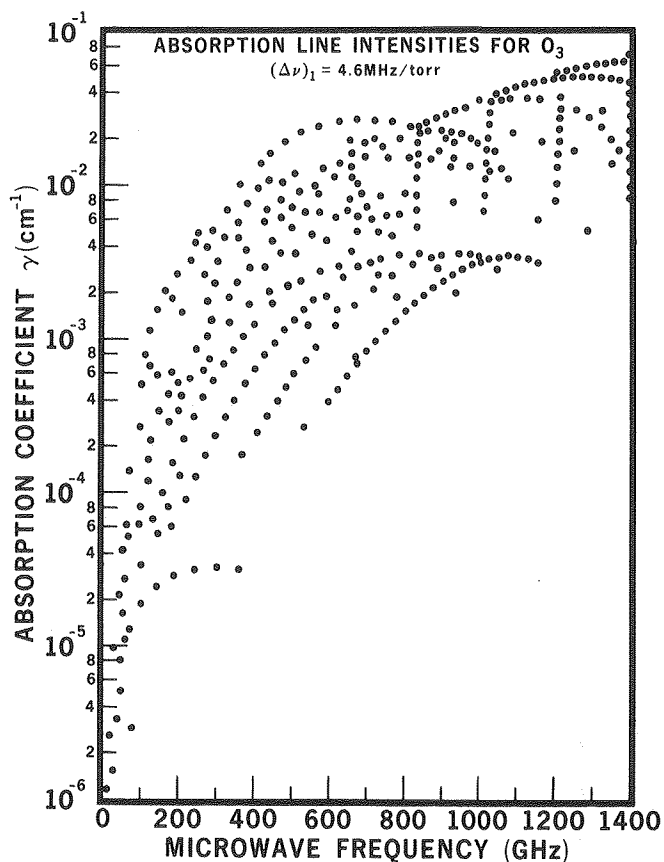


Fig. 5 Absorption coefficients for O_3 computed assuming $T = 300$ K, $(\Delta\nu)_1 = 4.6$ MHz/Torr, $f_v = 0.954$ and $i_c = 0.993$.

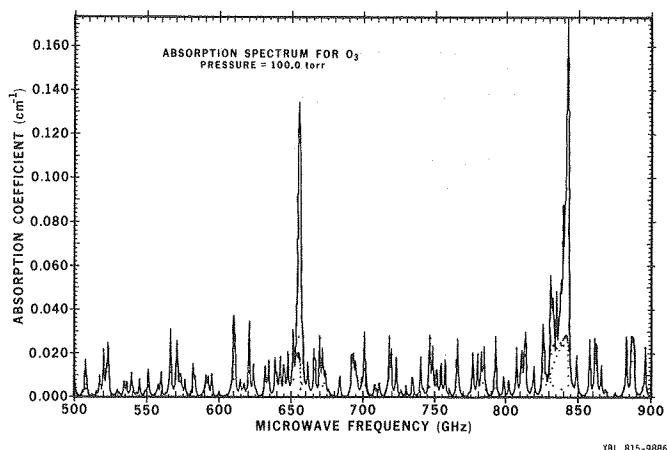


Fig. 6 Absorption spectrum for O_3 at a pressure of 100 Torr showing Q-branches in the frequency range of 500 to 900 GHz.

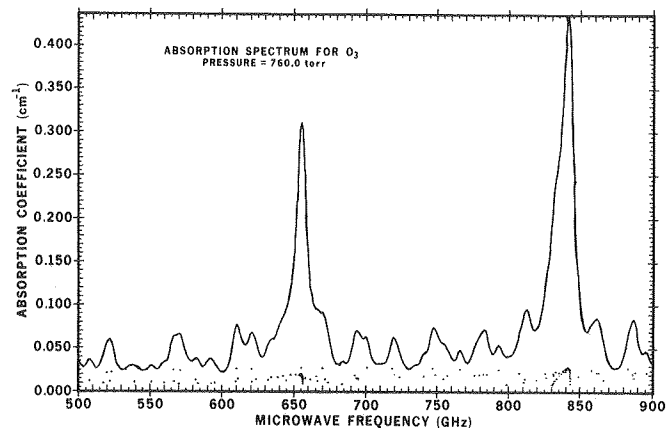


Fig. 7 Absorption spectrum for O_3 at a pressure of 760 Torr showing Q-branches in the frequency range of 500 to 900 GHz.

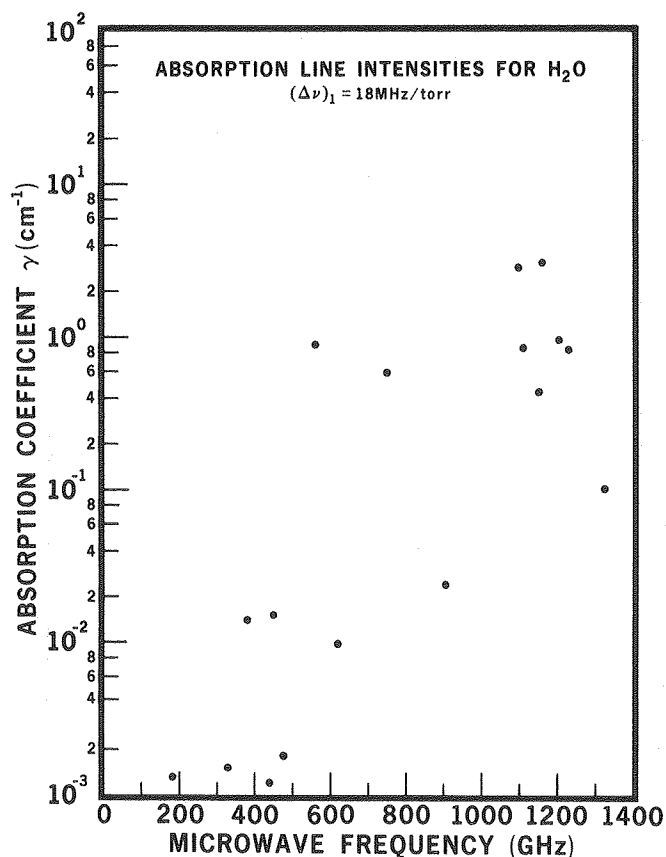


Fig. 8 Absorption coefficients for H_2O computed assuming $T = 300$ K, $(\Delta\nu)_1 = 18$ MHz/Torr, $f_v = 1.0$ and $i_c = 1.0$.

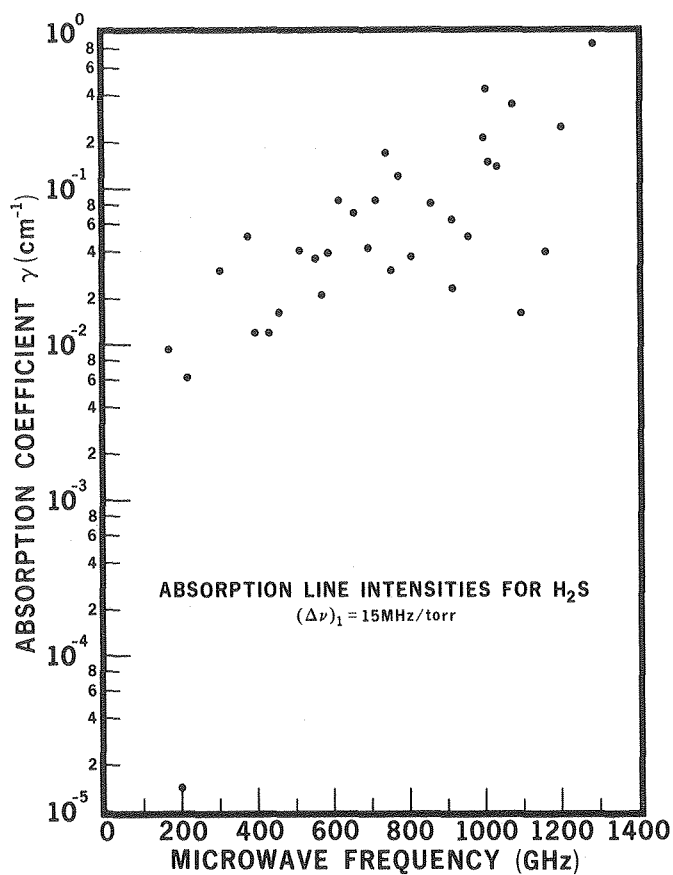


Fig. 9 Absorption coefficients for H_2S computed assuming $T = 300 \text{ K}$, $(\Delta\nu)_1 = 15 \text{ MHz/Torr}$, $f_v = 1.0$ and $i_c = 0.95$.

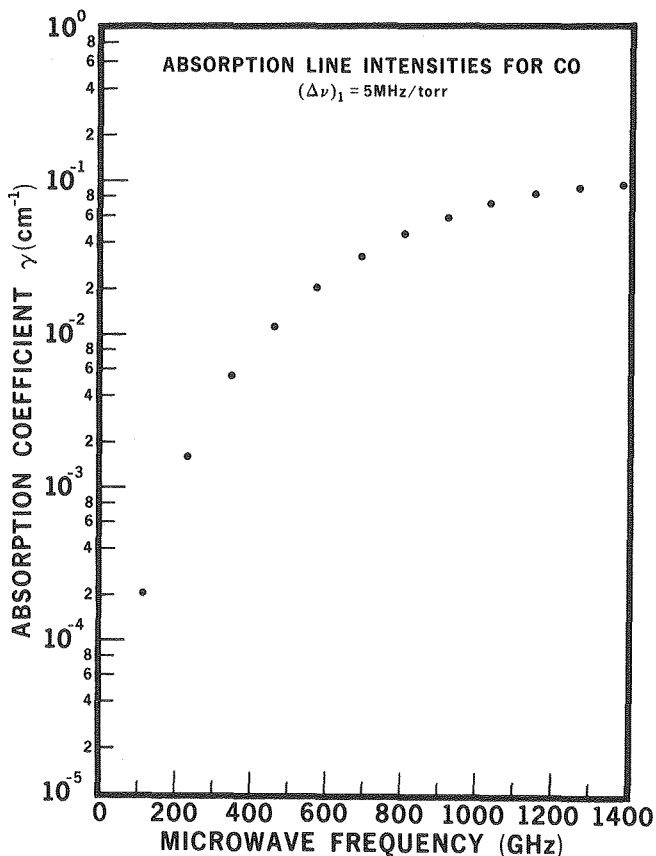
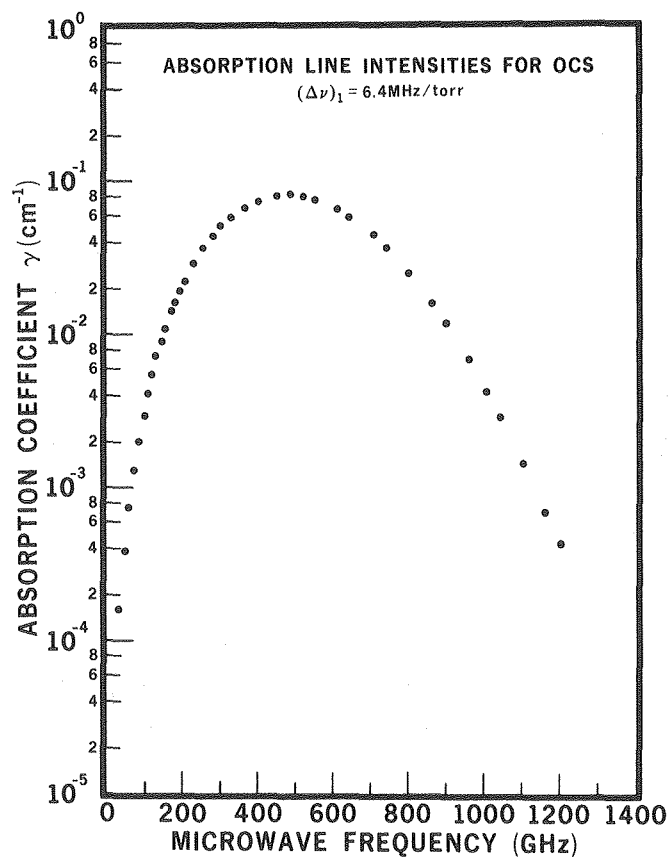
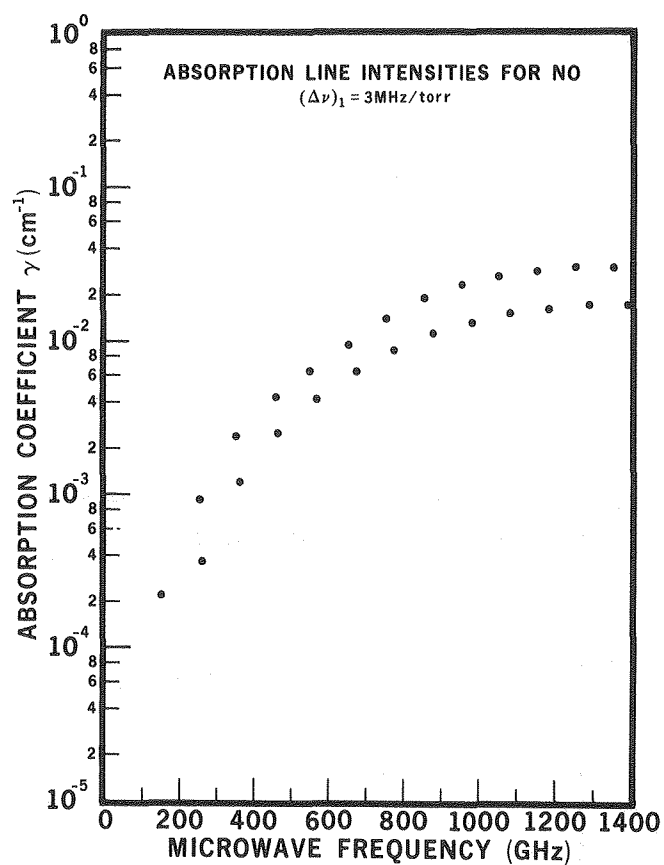


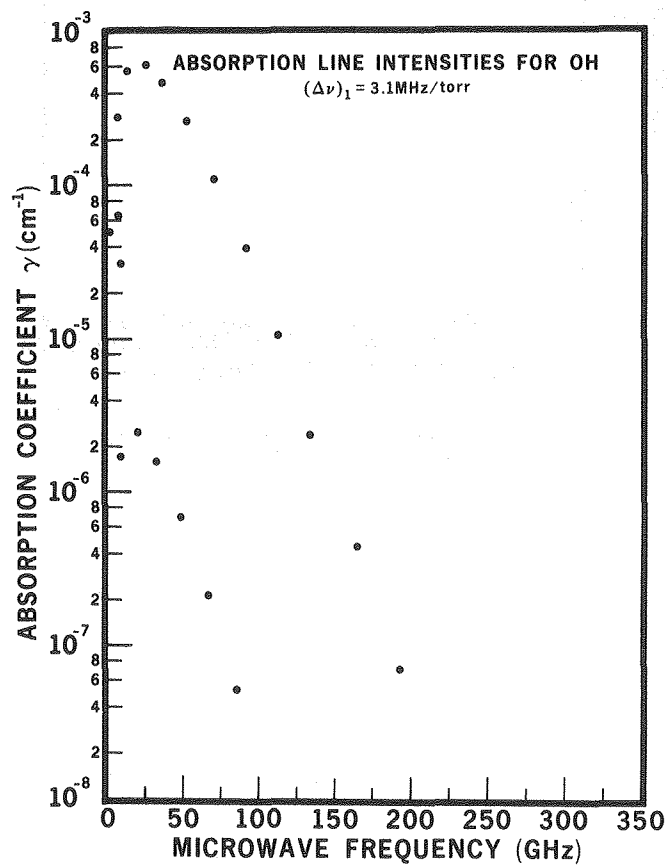
Fig. 11 Absorption coefficients for CO computed assuming $T = 300 \text{ K}$, $(\Delta\nu)_1 = 5 \text{ MHz/Torr}$, $f_v = 1.0$ and $i_c = 1.0$.

Fig. 10 Absorption coefficients for OCS computed assuming $T = 300 \text{ K}$, $(\Delta\nu)_1 = 6.4 \text{ MHz/Torr}$, $f_v = 0.83$, $i_c = 0.95$.



XBL 815-9892

Fig. 12 Absorption coefficients for NO computed assuming $T = 300$ K, ($\Delta\nu$)₁ = 3 MHz/Torr, $f_v = 1.0$ and $i_c = 1.0$.



XBL 815-9893

Fig. 13 Absorption coefficients for OH computed assuming $T = 300$ K, ($\Delta\nu$)₁ = 3.1 MHz/Torr, $f_v = 1.0$ and $i_c = 1.0$.

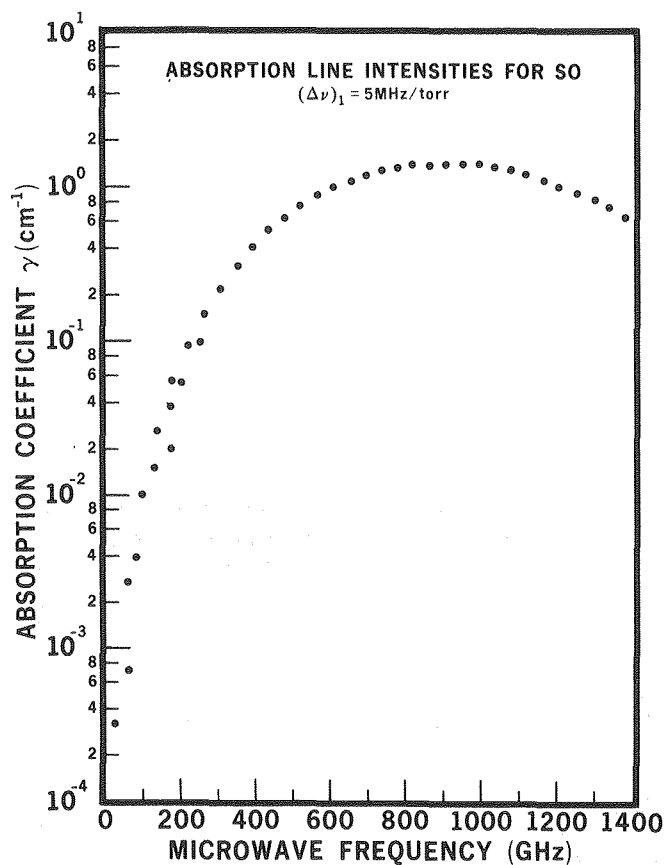


Fig. 14 Absorption coefficients for SO computed assuming $T = 300 \text{ K}$, $(\Delta\nu)_1 = 5 \text{ MHz/Torr}$, $f_v = 1$ and $i_c = 0.95$

XBL 815-9894

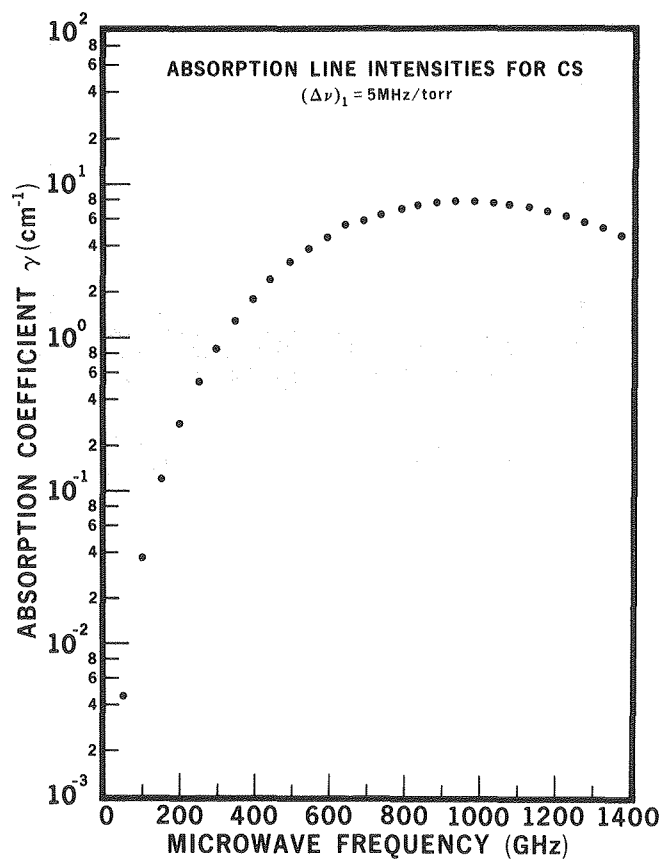


Fig. 15 Absorption coefficients for CS computed assuming $T = 300 \text{ K}$, $(\Delta\nu)_1 = 5 \text{ MHz/Torr}$, $f_v = 1$ and $i_c = 0.94$.

XBL 815-9895